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Synthesis of Ni_2H_3 at high temperatures and pressures

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In situ high-pressure high-temperature synchrotron x-ray diffraction studies of the nickel-hydrogen system reveals the synthesis of a nickel polyhydride, Ni_2H_3 . We observe the formation of NiH at pressures above 1 GPa, which remains stable to 52 GPa at room temperature. Laser heating to above 1000 K at this pressure initiates a transition to a phase which we determine as Ni_2H_3 , crystallizing in a body-centered monoclinic unit cell. The Ni_2H_3 phase was observed to convert back to NiH below 25 GPa, and upon further decompression to atmospheric conditions, NiH slowly releases hydrogen with time.

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The high-pressure synthesis and behavior of metal hydrides is an intensively studied topic of research due to the possibility of utilizing such materials for hydrogen storage purposes, and achieving predicted high-temperature superconducting states [1–3]. With the current consensus that reaching a metallic state of hydrogen remains outwith today's capabilities of diamond-anvil cell (DAC) experiments, research interests have shifted to hydrogen-dominant metallic alloys, which have also been predicted to exhibit exotic properties, such as high-temperature superconductivity [4–9]. To date the formation of hydrogen-bearing species has been theoretically explored for the majority of elements in the periodic table and recently, polyhydrides of first-row transition metals have been synthesized at high pressures [10–12]. However, there remains a gulf between the number of systems explored at pressures above 50 GPa and the extensive predictions in the literature.

The nickel-metal-hydride system has been extensively studied due to its importance as an alternative to Li-ion batteries [14]. As such, the majority of studies at pressure have been generally limited to conditions achievable by industry. Nickel has long been known to form a primary solid solution ($\gamma_1\text{-NiH}_x$ with $x \approx 0.01$) near ambient conditions formed by the absorption of atomic H into the Ni lattice [15,16]. As pressure is increased above 1.25 GPa and x approaches 1, Ni adopts a face-centered-cubic structure ($\gamma_2\text{-NiH}$) with $a = 3.731 \text{ \AA}$ (an expansion of the pure Ni fcc structure with $a = 3.5238 \text{ \AA}$) with H atoms occupying the octahedral sites [15,17,18]. The effects of pressure and hydrogenation on the magnetism of NiH have recently been explored through both experimental and theoretical methods [2,19,20]. However, no predictions of nickel polyhydride species have been reported to date.

Here we report, through a combination of x-ray diffraction experiments and density functional theory (DFT) calculations,

the synthesis and pressure-dependent behavior of a nickel polyhydride, Ni_2H_3 . This compound can be synthesized at pressures exceeding 52 GPa, and is stable on decompression to 21 GPa, below which it decomposes to the known monohydride, $\gamma_2\text{-NiH}$. Quenching the sample to atmospheric conditions, we find that $\gamma_2\text{-NiH}$ slowly releases molecular hydrogen over a period of 30 min as it decomposes to its constituent elements.

High-purity nickel powder (99.8%, 1.6 μm particle size) was loaded into DACs in an inert atmosphere, together with gold and/or ruby as a pressure marker and subsequently gas loaded with research-grade hydrogen gas (99.9999%) at 0.2 GPa [21,22]. Loading of hydrogen was confirmed by the observation of the hydrogen vibrational mode using a custom-built microfocused Raman system [6]. Rhenium gaskets were used to form the sample chamber in all experimental runs; diamond-anvil culets ranged from 200 to 300 μm , with sample sizes ranging between 50 and 125 μm once hydrogen was in the solid state. Angle-dispersive x-ray diffraction patterns were recorded on a fast image-plate detector with synchrotron radiation ($\lambda = 0.4131 \text{ \AA}$, 30 keV) at the BL10XU beamline, SPring-8, Japan [23]. Two-dimensional image-plate data were integrated with DIOPTAS to yield intensity vs 2θ plots [24]. Diffraction patterns were indexed with CONOGRAPH; Le Bail and Rietveld refinement was carried out in JANA2006 [25–28]. Total energy calculations were carried out within the framework of DFT in conjunction with the projector-augmented wave method and a plane wave basis, as implemented in the VASP code [29,30]. We used the optB88vdw exchange-correlation functional [31,32] and included the Ni 3*p*, 4*s*, and 3*d* electrons in the valence space. Pure hydrogen phase I was modeled in an eight-molecule cell of $P6_3/m$ symmetry. The plane wave cutoff energy was 800 eV and Brillouin zone sampling was done on regular *k*-point grids with separations of 0.025 \AA^{-1} .

After sample loading we observe the fcc structure of a primary solid solution $\gamma_1\text{-NiH}_x$ [$a = 3.5223(2) \text{ \AA}$ at 0.6 GPa]. On further compression above 1.0(5) GPa, the sample

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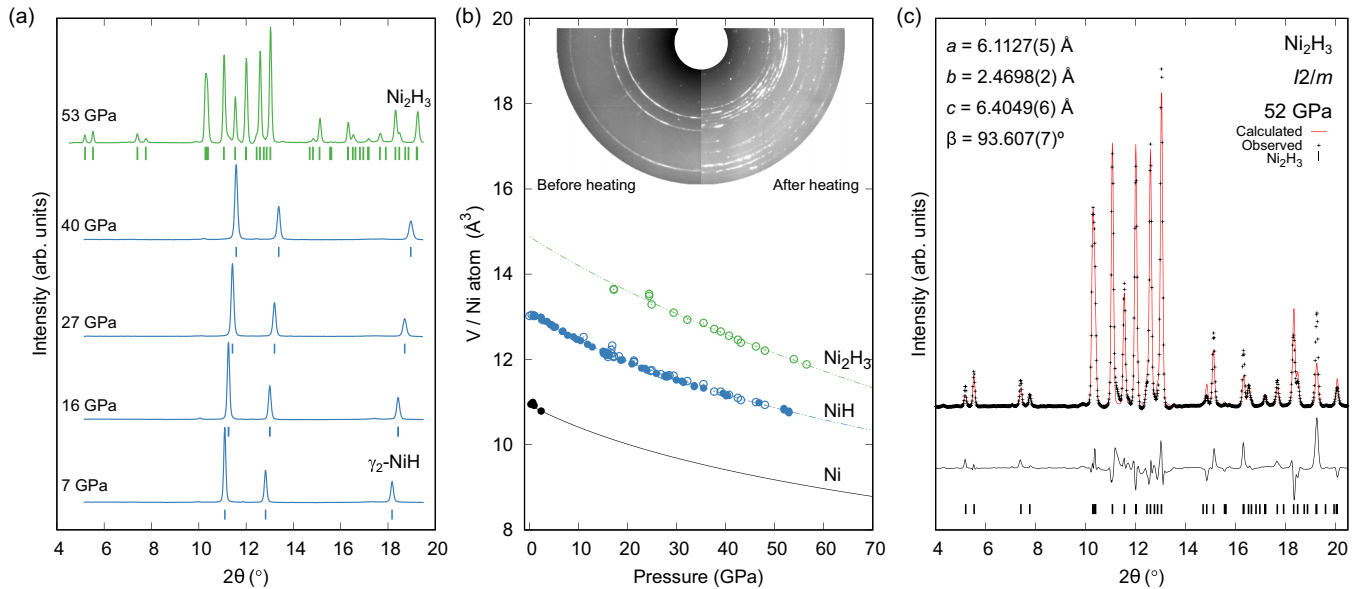


FIG. 1. (a) High-pressure x-ray diffraction patterns ($\lambda = 0.4131 \text{ \AA}$) showing the synthesis of Ni_2H_3 by laser heating above 50 GPa. Tick marks indicate the positions of Bragg reflections from the noted phases. (b) Atomic volume as a function of pressure for Ni (black), γ_2 -NiH (blue), and Ni_2H_3 (green). Fitted equations of state are shown with dashed lines; the equation of state of Ni is shown with a solid line [13]. Closed (open) symbols correspond to data collected on (de)compression. Inset shows raw image plates before and after laser heating showing the clear formation of textured rings due to Ni_2H_3 . (c) Representative Rietveld refinement of Ni_2H_3 data at 52 GPa with Ni atoms at $\text{Ni1}[0.7101(6), 0, 0.0640(6)]$ and $\text{Ni2}[0.0671(5), 0, 0.2439(6)]$, $wR_p = 1.94\%$, $wR_{\text{all}} = 14.19\%$.

transforms to the stoichiometric γ_2 -NiH phase indicated by the appearance of new diffraction peaks that could be indexed with an expanded fcc lattice, $a = 3.7329(1) \text{ \AA}$. This observation is in good agreement with previous measurements [16,19,33]. Neutron diffraction has shown the H atoms to occupy the larger octahedral vacancies in this phase, in a similar fashion to CoH and other transition-metal hydrides [10,17,34,35]. In the absence of heating, this structure remains stable on compression to at least 52 GPa, which is in good agreement with theoretical predictions [20].

In situ laser heating under compressed hydrogen has been successful in synthesizing new transition-metal compounds, particularly polyhydrides of Fe, Cr, and Co [10–12,36,37] and was applied here to explore the possibility of synthesizing nickel polyhydride species. Samples of γ_2 -NiH+ H_2 were compressed to 34, 40, and 52 GPa and laser heated at each pressure. Following laser heating at 40 GPa new peaks could be observed in the diffraction pattern; however, these new unexplained peaks disappeared on returning to ambient temperatures. At 52 GPa, *in situ* x-ray diffraction patterns show the disappearance of peaks due to γ_2 -NiH, which were replaced by numerous new peaks that remained on quenching (Fig. 1). Heating was localized to the NiH sample and temperatures were estimated to be less than 1000 K as no blackbody radiation was detectable from the sample during heating. All the observed peaks could be uniquely indexed to a body-centered monoclinic unit cell $a = 6.1137(3)$, $b = 2.4701(1)$, $c = 6.4019(3) \text{ \AA}$, and $\beta = 93.603(4)^\circ$ at 52 GPa [38]. Systematic absences were consistent with space groups without glide-plane symmetry elements and structure solution by charge flipping suggested space group $I2/m$ [39]. Despite extensive texturing of the diffraction rings, Rietveld refinement could be applied to several datasets giving reasonable

agreement factors in this space group. Ni-atom positions and thermal parameters could be refined, with two Ni-atom sites (see Fig. 1 caption for atomic positions).

Likely H-atom positions were identified using an electrostatic potential map based on DFT calculations of the Ni-atom unit cell. A range of possible stoichiometries were generated by the stepwise placement of H atoms, giving compositions from Ni_2H to Ni_4H_9 . Evaluating the relative enthalpies shows only a single stoichiometry, Ni_2H_3 , to become more stable than a combination of NiH and excess Ni or H_2 : above 54.8 GPa Ni_2H_3 is more stable than $2 \text{ NiH} + \frac{1}{2} \text{ H}_2$; by 60 GPa the formation enthalpy is $-11.6 \text{ meV/Ni}_2\text{H}_3$. The optimized structure from DFT calculations is shown in Fig. 2; unit-cell dimensions and structural parameters are given in Table I. There are two unique Ni-atom positions coordinated by eight and seven H atoms, respectively, forming irregular polyhedra. Direct comparison of Ni-H bond distances between γ_2 -NiH at the same pressure shows that the synthesis of Ni_2H_3 leads to an increase in coordination number without a significant

TABLE I. Atomic position parameters refined by DFT for Ni_2H_3 at 55 GPa, $a = 6.110$, $b = 2.467$, $c = 6.416 \text{ \AA}$, $\beta = 93.37^\circ$, space group $I2/m$.

Atom	Site	x	y	z
Ni1	4i	0.71014	0	0.06893
Ni2	4i	0.07325	0	0.24375
H1	2d	0	0	$\frac{1}{2}$
H2	2a	0	0	0
H3	4i	0.61809	0	0.30373
H4	4i	0.30209	0	0.38897

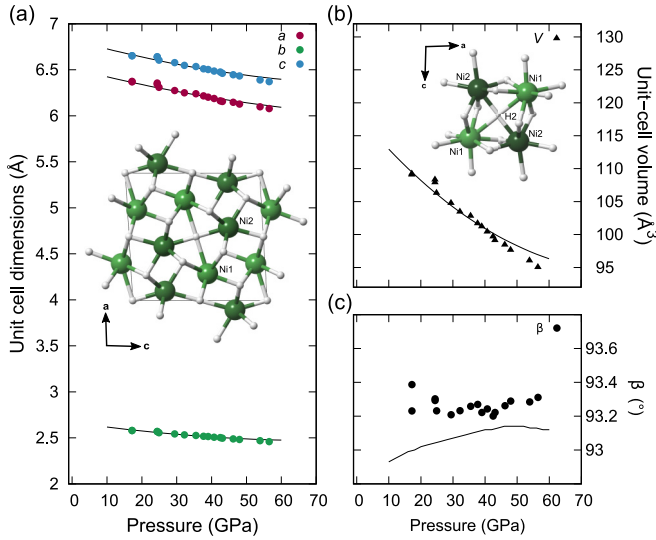


FIG. 2. (a) Ni_2H_3 unit-cell dimensions as a function of pressure. Inset: Crystal structure of Ni_2H_3 which crystallizes in space group $I2/m$ with two unique Ni atoms. (b) Ni_2H_3 unit-cell volume as a function of pressure. Inset: Ni_2H_3 structure showing four-coordinated H atoms in a distorted square planar arrangement. (c) Monoclinic angle, β , as a function of pressure. Data points in (a)–(c) are from experiments while lines correspond to values derived from DFT calculations at 0 K.

decrease in Ni-H bond distances. The structure of Ni_2H_3 partially retains the Ni_4H_4 cubic units of $\gamma_2\text{-NiH}$ but in distorted form, additional H atoms (H2) are coordinated by four Ni atoms forming distorted squares in the ac plane, breaking up the regular fcc lattice [inset, Fig. 2(b)]. The emergence of lower H-atom coordination has been predicted in several transition-metal hydrides and may lead to the formation of H-atom layers with increasing pressure and hydrogen content [11,40,41]. Over the stability range of Ni_2H_3 there is close agreement between the experimentally observed unit-cell dimensions and those derived from DFT calculations (Fig. 2), supporting our assignment of the hydrogen content. However, this should be experimentally verified by high-pressure neutron diffraction. The pressure-volume behaviors of NiH and Ni_2H_3 were fitted with third-order Birch-Murnaghan equations of state giving the parameters shown in Table II.

Magnetism was considered in the calculations for pure Ni, but not for the hydrides; a magnetic calculation of the $\gamma_2\text{-NiH}$ rapidly demagnetized at all pressures. It is not clear whether this is an artifact of DFT preferring nonmagnetic solutions

TABLE II. Birch-Murnaghan equation of state parameters for Ni [13], $\gamma_2\text{-NiH}$, and Ni_2H_3 . B'_0 was freely refined for both NiH and Ni_2H_3 .

Phase	V_0 (Å ³ /Z)	B_0 (GPa)	B'_0
Ni [13]	10.9315	181	5.2
$\gamma_2\text{-NiH}$ (this work)	13.06(24)	191(10)	3.8(4)
$\gamma_2\text{-NiH}$ [19]	13.14(2)	176(2)	4 (fixed)
Ni_2H_3	14.9(19)	204(43)	2.2(9)

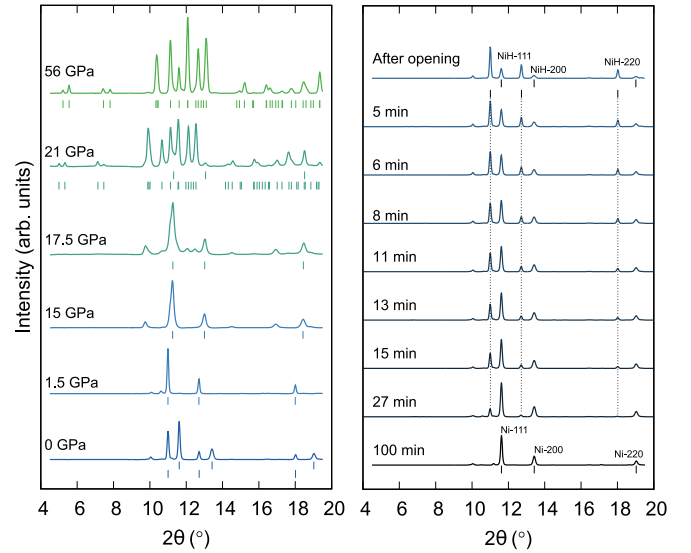


FIG. 3. High-pressure x-ray diffraction patterns ($\lambda = 0.4131$ Å) taken on decompression showing (left) the stepwise decomposition of Ni_2H_3 into $\gamma_2\text{-NiH}$ and (right) the subsequent decomposition of $\gamma_2\text{-NiH}$ into Ni and H_2 at ambient pressure.

or if metal hydrides are inherently nonmagnetic. Note that recent structure predictions in a similar system, Cr-H, also exclusively find nonmagnetic hydrides [42]. Either way, this should not affect the stability of Ni_2H_3 against $\gamma_2\text{-NiH}$ and H_2 .

As can be seen in Fig. 3, on decompression below 25 GPa, weak peaks corresponding to $\gamma_2\text{-NiH}$ begin to appear, and by 17.5 GPa, they fully replace those of Ni_2H_3 . Reflections from $\gamma_2\text{-NiH}$ could be observed down to ambient pressure and continue to remain upon opening the diamond-anvil cell to atmospheric conditions. Once quenched, we see the appearance of diffraction peaks corresponding to pure Ni and these reflections grow with time as the reflections from $\gamma_2\text{-NiH}$ decrease in intensity. After approximately 1 h, no reflections due to $\gamma_2\text{-NiH}$ could be observed leaving only those due to Ni (see Fig. 3).

The recovery of $\gamma_2\text{-NiH}$ to low pressures (0.34 GPa) at room temperature, and recovery to ambient pressure at low temperatures (85 K) have been observed before [43–45]. The metastable preservation to ambient pressure at room temperature is unexpected and the reason for this is not fully understood. The transition from $\gamma_1\text{-NiH} + \text{H}_2$ to $\gamma_2\text{-NiH}$ is known to be sluggish so it is likely that the transition from $\gamma_2\text{-NiH}$ to $\text{Ni} + \text{H}_2$ is also kinetically hindered which resulted in the continued presence of the $\gamma_2\text{-NiH}$ structure at ambient pressure [45]. As the hydrogen content of the structure cannot be directly determined from our x-ray diffraction data, future large-volume neutron diffraction experiments exploring the synthesis and quench are imperative toward the consideration of $\gamma_2\text{-NiH}$ as a hydrogen storage medium.

In conclusion, we have explored the Ni-H system up to pressures of 60 GPa with combined x-ray diffraction and laser heating. With this method we have synthesized a Ni_2H_3 species by reaction of $\gamma_2\text{-NiH}$ and H_2 at pressures above 50 GPa. Ni_2H_3 remains stable down to approximately 17 GPa

before transforming to γ_2 -NiH. At ambient temperatures γ_2 -NiH can be quenched to atmospheric pressure whereupon it releases H_2 as it slowly transforms into pure Ni.

Note added. Recently, an independent study described the prediction and subsequent experimental observation of the same Ni_2H_3 compound [46]. Their reported synthesis pressure (60 GPa) is higher than in this study (52 GPa); however,

the decomposition pressure, unit-cell dimensions, and derived equation of state parameters are in close agreement with our data [46].

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